It has already appeared that experiment gives for I in No. 1  $2.3 \times 10^6$ , and in No. 2  $2.65 \times 10^6$ . The difference is probably due to error in estimating the lead of the brushes, which is difficult, owing to uncertainty in the position of the neutral line on open circuit.

II. "On the Clark Cell as a Standard of Electromotive Force."
By R. T. GLAZEBROOK, M.A., F.R.S., Fellow of Trinity
College, and S. SKINNER, M.A., Christ's College, Demonstrator in the Cavendish Laboratory, Cambridge. Received
February 17, 1892.

# (Abstract.)

The paper consists of two parts:—

In Part I an account is given of experiments on the absolute electromotive force of a Clark cell.

This was determined in the manner described by Lord Rayleigh ('Phil. Trans.,' 1884) in terms of a known resistance and the electrochemical equivalent of silver.

The resistance used was a strip of platinoid about 1 cm. wide and 0.05 cm. thick wound on an open frame. It was immersed in a bath of paraffin oil, and the currents used, varying from about 0.75 to rather over 1.4 ampères, did not raise its temperature sufficiently to affect the result. It had a resistance of nearly 1 B.A. unit. This was determined in terms of the original B.A. units. As part of the object of the experiments was to test the memorandum on the use of the silver voltameter recently issued by the Electrical Standards Committee of the Board of Trade, the large currents mentioned above were purposely employed. The silver voltameters were treated in accordance with the instructions in the memorandum.

The standard cell to which the results are referred is one constructed by Lord Rayleigh in 1883, probably No. 4 of the cells described in his paper already quoted.

The results have been reduced on the supposition that 1 B.A. unit is equal to 0.9866 ohm; if we take the number 0.9535\* as representing the value in B.A. units of the resistance of a column of mercury at 0°, 1 metre long, 1 sq. mm. in section, the above is equivalent to saying that the length of the mercury column having a resistance of 1 ohm is 106.3 cm. It has also been assumed that the mass of silver deposited in one second by a current of 1 ampère is 0.001118 gramme, and that the coefficient of change of E.M.F. with temperature of a Clark's cell is 0.00076. This last result has been verified by us in Part II.

\* This number is the mean of the best recent results.

An account of nine separate experiments is given in the paper; the following are the results reduced to 15° C.:—

No. of experiment.	E.M.F. of cell.	No. of experiment.	E.M.F. of cell.		
1 2 3 4 5	1 ·4341 1 ·4336 1 ·4341 1 ·4340 1 ·4340	6 7 8 9	1 · 4342 1 · 4342 1 · 4340 1 · 4345		

The mean of these is 1 4341, or, correcting for the rate of the clock, 1 4342.

In Experiment 2 the current in the voltameter was rather unsteady, which may account for the low value; while in Experiment 9 the temperature of the cell was changing somewhat, and our later experience has shown us that the E.M.F. in our standard cell lags very considerably behind the temperature. Still even taking these experiments into account, the results are very close.

If we suppose, as seems most probable, for reasons given in the paper, that our cell is No. 4 of Lord Rayleigh's paper, and that it has retained relative to No. 1 (Lord Rayleigh's standard) the value it had in 1883, the E.M.F. of his cell No. 1 would be in the units he used

## 1.4346 volts at 15°.

The value found by Lord Rayleigh was 1.4348 volts; thus the two are very close.

In the units we have given above, those specified by the Board of Trade, we have finally the result that the E.M.F. of our cell is

1.4342 volts at 15° C. or 1.4324 volts at 62° F.

#### PART II.

In the second part of the paper we have investigated some of the sources of error in the Clark cell, and also the effects of small variations in the materials used and the method of their preparation. We have also compared a number of cells set up by different makers. The general result is a very good agreement among cells from very various sources.

Cells set up by Lord Rayleigh in 1883 and 1884, Mr. Elder in 1886, Mr. H. L. Callendar in 1886, Dr. Muirhead in 1890, and by Dr.

Schuster, Mr. Wilberforce, and ourselves during the past year, all agree closely, the variations among them being rarely greater than about 0.0005 volt.

The first set of cells, eighteen in number, constructed for the purposes of this enquiry were made according to Lord Rayleigh's instructions, using, however, various specimens of the chemicals. These showed some differences at first, but in the course of about two months they had all, with one exception, settled down to close agreement with the standard. The exceptional cell has since become normal. In two of these cells mercury was used which had been taken direct from the stock in every-day use in the laboratory. The E.M.F. of these cells was much too low at first, but it gradually increased, and they are now normal. The mercurous sulphate appears to free the mercury from certain harmful impurities.

Another set of cells were put up, in accordance with the provisional memorandum of the Electrical Standards Committee of the Board of Trade, issued in June last and quoted below.

MEMORANDUM ON THE PREPARATION OF THE CLARK'S STANDARD CELL.

## Definition of the Cell.

The cell consists of mercury and zinc in a saturated solution of zinc sulphate and mercurous sulphate in water, prepared with mercurous sulphate in excess, and is conveniently contained in a cylindrical glass vessel.

#### Preparation of the Materials.

- 1. The Mercury.—To secure purity it should be first treated with acid in the usual manner, and subsequently distilled in vacuo.
- 2. The Zinc.—Take a portion of a rod of pure zinc, solder to one end a piece of copper wire, clean the whole with glass paper, carefully removing any loose pieces of the zinc. Just before making up the cell, dip the zinc into dilute sulphuric acid, wash with distilled water, and dry with a clean cloth or filter paper.
- 3. The Zinc Sulphate Solution.—Prepare a saturated solution of pure ("pure recrystallised") zinc sulphate by mixing in a flask distilled water with nearly twice its weight of crystals of pure zinc sulphate, and adding a little zinc carbonate to neutralise any free acid. The whole of the crystals should be dissolved with the aid of gentle heat, i.e., not exceeding a temperature of 30° C., and the solution filtered, while still warm, into a stock bottle. Crystals should form as it cools.
- 4. The Mercurous Sulphate.—Take mercurous sulphate, purchased as pure, and wash it thoroughly with cold distilled water by agitation in a bottle; drain off the water, and repeat the process at least twice. After the last washing, drain off as much of the water as possible.

Mix the washed mercurous sulphate with the zinc sulphate solution, adding sufficient crystals of zinc sulphate from the stock bottle to ensure saturation, and a small quantity of pure mercury. Shake these up well together to form a paste of the consistency of cream. Heat the paste sufficiently to dissolve the crystals, but not above a temperature of 30°. Keep the paste for an hour at this temperature, agitating it from time to time, then allow it to cool. Crystals of zinc sulphate

should then be distinctly visible throughout the mass; if this is not the case, add more crystals from the stock bottle, and repeat the process.

This method ensures the formation of a saturated solution of zinc and mercurous sulphates in water.

The presence of the free mercury throughout the paste preserves the basicity of the salt, and is of the utmost importance.

Contact is made with the mercury by means of a platinum wire about No. 22 gauge.—This is protected from contact with the other materials of the cell by being sealed into a glass tube. The ends of the wire project from the ends of the tube; one end forms the terminal, the other end and a portion of the glass tube dip into the mercury.

### To set up the Cell.

The cell may conveniently be set up in a small test-tube of about 2 cm. diameter, and 6 or 7 cm. deep. Place the mercury in the bottom of this tube, filling it to a depth of, say, 1.5 cm. Cut a cork about 0.5 cm. thick to fit the tube; at one side of the cork bore a hole, through which the zinc rod can pass tightly; at the other side bore another hole for the glass tube which covers the platinum wire; at the edge of the cork cut a nick through which the air can pass when the cork is pushed into the tube. Pass the zinc rod about 1 cm. through the cork.

Clean the glass tube and platinum wire carefully, then heat the exposed end of the platinum red hot, and insert it in the mercury in the test-tube, taking care that the whole of the exposed platinum is covered.

Shake up the paste and introduce it without contact with the upper part of the walls of the test-tube, filling the tube above the mercury to a depth of rather more than 2 cm.

Then insert the cork and zinc rod, passing the glass tube through the hole prepared for it. Push the cork gently down until its lower surface is nearly in contact with the liquid. The air will thus be nearly all expelled, and the cell should be left in this condition for at least twenty-four hours before sealing, which should be done as follows:—

Melt some marine glue until it is fluid enough to pour by its own weight, and pour it into the test-tube above the cork, using sufficient to cover completely the zinc and soldering. The glass tube should project above the top of the marine glue.

The cell thus set up may be mounted in any desirable manner. It is convenient to arrange the mounting so that the cell may be immersed in a water-bath up to the level of, say, the upper surface of the cork. Its temperature can then be determined more accurately than is possible when the cell is in air.

These cells, as the tests given show, have been good from the first, and, indeed, we have not had any difficulty with any of the cells in which the instructions of this memorandum have been followed.

The mercury used had been distilled in the laboratory, the zincs were supplied as "pure" by Messrs. Harringtons, of Cork, while the zinc and mercurous sulphates came from Messrs. Hopkin and Williams.

The numbers in the table show the differences between the cells and the standard; the unit is 0.00025 volt.

Differences between a Set of Cells and the Standard.

July 18.*	15	4-	21	61	63	61	က
July 7.*	15	2	က	-	4	4	81
Dec. 17.	15	-2	Н	0	7	ī	0
Nov. 14.	9.5	-2		-			0
Nov. 2.	14.4	-	Н	Н	П	П	-
Aug. 22.	16.4	0	0	0	0	H	ī
Aug. 14.	17.5	0	0	H	0	Н	2
Aug. 10.	16.4	0	0	0	0	0	0
Aug. 6.	16.2	0	1	П	1	Н	-1
July 20.	18	0	H	H	67	0	0
June 9.	14.5	ī	7	∞ 1	67	0	-1
June 6.	16	ī	ij	8	-	Ï	63
June 4.	16	4-	က	8	1.2	1.5	6
Date June 4. June 6. June 9. July 20. Aug. 6. Aug. 10. Aug. 14. Aug. 22. Nov. 2. Nov. 14. Dec. 17. July 7.* July 18.*	Temperature	No. 71	,, 72	,, 73	,, 74	" 75	" 76

\* Comparison with the standard of the Board of Trade. The unit is 0.00025 volt.

It may be well to explain the purpose of some of the precautions advised in the circular. The mercurous sulphate, as ordinarily purchased, contains some mercuric sulphate. When this is moistened with water it is resolved into a yellow basic mercuric sulphate (turpeth mineral) and a soluble acid mercuric sulphate. The first, at any rate in moderate quantities, does not affect the E.M.F.; the latter greatly hinders it from attaining the proper value. Repeated washing, however, removes most of this soluble salt. The paste, when made, is shaken with mercury to remove any traces of the acid sulphate which may be left, for the acid mercuric sulphate attacks the mercury and forms mercurous sulphate.

Careful precautions are necessary to ensure that the solutions should be saturated with both zinc and mercurous sulphates, but the solutions should not be raised in temperature above 30° C., for the zinc sulphate may then crystallise out in the wrong form. The proper crystals have the composition ZnSO<sub>4.7</sub>H<sub>2</sub>O, and are rhombic.

But while we have had no serious difficulty with any of the cells prepared in accordance with the last form of the memorandum, some of the other cells we have set up have led to some interesting results.

Two sets of cells were put up with great care by Mr. Wilberforce in March and April. One of us (S. S.) set up some cells in the same way about the same time. The solutions were prepared from very pure materials, following Lord Rayleigh's instructions. The zinc sulphate was remarkably free from acid, and it appeared as if the results ought to be good.

In the first set, Nos. 36—41, the E.M.F. was too low. At the end of a month it was much too low, about 0.005 volt, and Mr. Wilberforce noticed that a dull-grey deposit covered the zines; he therefore removed them and scraped off this deposit, when, on replacing the zines, the cells were found to have approximately the normal E.M.F.; they have continued nearly normal since. The next set, Nos. 42—47, were very good when first set up, but the E.M.F. soon fell rapidly, until at the end of a month they were nearly 0.01 volt too low.

The grey deposit again was formed over the zinc. Some of these cells were left untouched till August, by which time the E.M.F. had recovered somewhat, being then about 0 005 too low. Others had been treated by removing the zincs and replacing them by amalgamated zincs. In August some experiments were made on the unaltered cells, which showed conclusively that it is necessary that the surface of the zinc should remain bright if consistent results are to be obtained.

This bright surface may be secured by amalgamating the zinc, but we are not yet sure that this alone is effective, for it seems possible from various observations that some action which results in the amalgamation of the zinc must go on in the cell to enable it to reach the steady state, and that it may not be sufficient to introduce amalgamated zincs. On this and some kindred points, however, we are still experimenting. The grey deposit can be shown to be mainly mercury in a state of very fine division. There are some indications that a slight acidity in the solutions is of use in promoting amalgamation.

We have verified repeatedly an observation of Dr. Hopkinson's that the E.M.F. of a bad cell changes considerably if the cell be slightly shaken, while that of a good cell is not affected.

The paper also contains an account of some experiments on the coefficient of change of E.M.F. with temperature. The value found is 0.000755 per 1°C., practically the same as that given by Lord Rayleigh. In this connexion we may mention the important observation that when the temperature is rising, even although the rise be only a few degrees, the E.M.F. of the cell may—especially if the cell be large-lag very considerably behind the temperature. On one occasion in which the temperature rose by some 5°C. in about a week, the E.M.F. of our large cell at the end of the week corresponded to a temperature nearly 3° lower than that given by a thermometer in the bath with the cell, being about 0.0027 volt too high. In this case a thick cake of crystals had formed on the top of the more solid portion of the paste, and the zinc sulphate solution only attained the state of saturation corresponding to the temperature by very slow degrees. Mr. Carhart and Mr. Swinburne have called attention to the difficulties which thus attend the practical use of the cells. They are to some extent met by using small cells.

The paper also describes a new form of portable cell which may be turned into any position without harm. Experiments have also been made on the mercury chloride standards described by Von Helmholtz. A set of these has been constructed which has an E.M.F. of very nearly 1 volt. A form of standard due to Gouy, in which oxide of mercury is used, has also been examined. The E.M.F. of these cells prepared with yellow oxide is, we find, 1.381 volts, and when prepared with red oxide 1.388 volts.

By the kindness of Major Cardew several of our cells have been compared with the standards of the Board of Trade. The differences are very small, being about 0.0003 volt. The average of the Board of Trade cells is less than our standard by about this amount.

The Board of Trade possess seventy-two cells, and Mr. Rennie, Major Cardew's Assistant, informs us that the greatest difference between any two of them is under 0.0007 volt. It will be seen from the table given that, while the cells there considered are on the average about one of our units above our standard, they are rather over two of such units above the Board of Trade cells.

Thus our standard exceeds the cells of the Board of Trade by rather over one of our units, or about 0.0003 volt.

If we take the E.M.F. of our standard as 1.4342 volts at 15°, the cells of the Board of Trade average in E.M.F. about 1.4339 volts at 15° C., or 1.4321 volts at 62° Fahr.

III. "Note on the Functional and Structural Arrangement of Efferent Fibres in the Nerve-roots of the Lumbo-sacral Plexus." (Preliminary Communication.) By C. S. Sher-RINGTON, M.A., M.B., &c. Communicated by Professor M. FOSTER, Sec. R.S. Received March 14, 1892.

At the commencement of some observations on the reflex mechanisms of the spinal cord in *Macacus rhesus*, difficulties were encountered which made it desirable to attempt for that animal a somewhat particular examination of the distribution of the efferent and afferent spinal nerve-roots belonging to the lumbo-sacral plexus. The present communication has reference to the distribution of the efferent fibres of the roots.

Reil,\* Scarpa,† A. Monro, † and Soemmering all paid considerable attention to the arrangement of the root-bundles in the limb plexuses, but physiological work upon the subject commenced with Van Deen, J. Müller, ¶ and Panizza.\*\* The former two gave an anatomical significance to the plexus, the last a physiological. At Müller's suggestion, renewed research was undertaken by H. Kronenberg†† in 1835. Kronenberg confirmed Müller's observations as to the individual inconstancy of the contribution made by any spinal root to the nerve cords of the plexus; he also concluded that the excitation of a single nerve-root before its entrance into the plexus produces contraction of almost all the muscles of the limb; and that the arrangement is intended to protect against fatigue. Eckhardt, 11 working in Ludwig's laboratory, arrived at somewhat similar conclusions. He stated that a great number of muscles obtain nerve-fibres each of them from several nerve-roots; that there is a good deal of individual variation; that when a nerve-root is

- \* 'De Nervorum Structura,' p. 14.
- + 'De Gangliis et Plexibus.'
- ‡ 'Observations on the Structure and Functions of the Nervous System,' p. 34.
- § 'Anatom.,' Pars Vta.
- || 'De Differentia et Nexu inter Nervos Vitæ Anim. et Organ.,' Leyden, 1834.
- ¶ 'Physiol. des Menschen,' vol. 2, p. 586.
- \*\* 'Annali Universali di Medicina.'
- †† Essay ('De Struct. et Virtut. Plexuum Nervorum'), Berlin, 1836.
- 11 'Zeits. f. Rat. Med.,' vol. 7, p. 306, 1849.